METHANE CLATHRATE: DIRTY FUEL OR ENERGY SAVIOR: A NEW FORM OF ICE TO STORE ENERGY

Shashi Kumar[1]

[1]*M.Tech, Department of Chemical Engineering, Indian School of Mines Dhanbad- 826004, Jharkhand-India.*

Abstract

Methane hydrates are ice-like materials, which form at low temperature and high pressure and are located in permafrost areas and oceanic environments. They represent a huge hydrocarbon resource, which could supply the entire world for centuries. Clathrate hydrates were considered for many years as harmful by the oil and gas industry because of their annoying tendency to plug pipelines and damage to internal pipeline structure. However, they are now attracting renewed interest in many fields. Scientific knowledge of natural clathrate hydrates has grown enormously over the past decade with spectacular new findings of large exposures of complex hydrates on the sea floor and significant progress in modeling natural hydrate systems. Other positive applications include carbon dioxide sequestration, separation and natural gas storage and transportation. Major unresolved questions remain about the role of hydrates in response to climate change today and about the viability of marine hydrates as an economic resource. Finally, the use of their dissociation energy can be applied in refrigeration processes and cool storage. New and energetic explorations by nations such as India, China, Japan and other are quickly uncovering large hydrate findings on their continental shelves.

Key Words: Clathrate hydrate, Carbon dioxide Sequestration, Cool storage, Separation, Pipeline Plugging, Environment, Hydrocarbon, Permafrost, Refrigeration, Explorations.

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1. INTRODUCTION

Since 'Clathrate' were initially discovered by Sir Davy Humphrey in 1810, natural gas hydrates as potential energy resource for the future. For many decades, countries such as the USA, Japan, India, and China have funded major research projects to get a better knowledge and understanding of natural gas hydrates [1]. Resource assessment studies have demonstrated the huge potential of gas hydrate accumulations as a future energy resource [2]. World energy demand is continues rising due to global population and economic growth. The total increase in world energy consumption is increase to 44% from 2006 to 2030 [3]. China and India are currently the fastest growing economies and their combined energy consumption is expected to represent 28% of the world energy consumption in 2030 [4]. Despite recent progress in obtaining energy from non-fossil fuels, nearly 80% of the world energy supply will still be generated from oil, natural gas and coal. Their combustion is a major source of carbon dioxide emissions. Unfortunately, a perceived change in the global climate has been attributed to the increasing concentration of Green House Gases such as CO_2 in the atmosphere [5]. Sequestration of CO_2 in marine and arctic hydrates is considered as an advanced geologic sequestration concept, which needs further investigation [6]. Gas hydrates are found in nature in permafrost and marine environments. They contain mixtures of gases such as methane and ethane, with carbon dioxide and hydrogen sulfide as trace. Methane is the predominant component of natural gas hydrates, which is the reason they are simply called methane hydrates. Gas hydrates form under specific conditions: (1) the right combination of pressure and temperature (high pressure and low temperature), (2) the presence of hydrate-forming gas in sufficient amounts, and (3) the presence of water. However, the resource for recovery of gad hydrates is still not commercially viable due to technical, environmental, and economic issues. Any further investigation of the mixed CO_2 – CH_4 gas hydrate properties could lead to major breakthroughs in the fields of unconventional resource production and carbon sequestration. Intense research on natural gas hydrates was conducted by the oil and gas industry when it was pointed out that these compounds were responsible for plugging natural gas pipelines [7]. In fact, light gases such as methane or ethane present in petroleum products are easily trapped as guest molecules in hydrate structures [8-10]. Finally, clathrate hydrates offer high latent heats of dissociation that can be utilized for refrigeration applications, such as cold storage or air conditioning [11, 12].

2. Methane Clatharate: What are they?

The term 'clathrate', meaning barrier indicates crystalline inclusion compounds in which small guest atoms or molecules are physically trapped in host cavities shaped by a three dimensional assembly of hydrogen bonded molecules. These compounds are called clathrate hydrates. Methane clathrate ($CH_4 \cdot 5.75H_2O$) or ($4CH_4 \cdot 23H_2O$), also called methane hydrate, hydro methane, methane ice, fire ice, natural gas hydrate, or gas hydrate, is a solid clathrate compound (more specifically, a clathrate hydrate [13]. Now, "clathrate" is mostly used when discussing the molecular

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structure of these minerals, whereas the term clathrate" is best used when discussing accumulations of these minerals in a sedimentary bed. The general formula for a methane hydrate is CH_4 and H_2O where "n", describes a variable number of water molecules within the lattice structure. Originally thought to occur only in the outer regions of the Solar System, where temperatures are low and water ice is common, significant deposits of methane clathrate have been found under sediments on the ocean floors of the Earth [14]. According to the size of the trapped molecule, three types of structures are observed: cubic I [15], cubic II [16] and hexagonal H [17]. These structures correspond to different arrangements of the water molecules. These gas clathrates are partially held together by pressure, so they cannot exist in marine sediments above about 250 meters deep. We understand that methane hydrates are formed when methane and other gases that come from decaying organic material become trapped in a clathrate crystal lattice within a defined zone of stability near the ocean. **Figure-1** shows the Burning ice: Methane, released by heating.

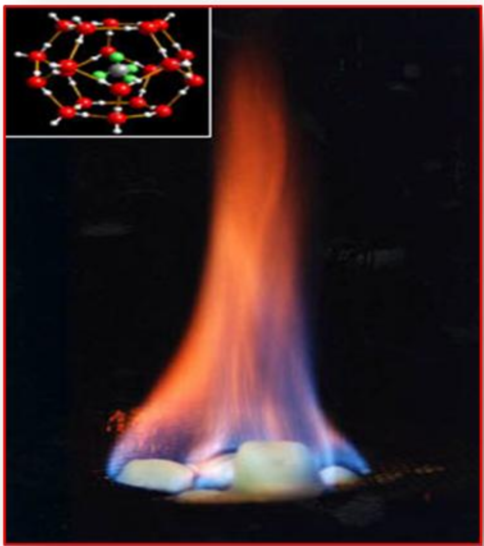

Figure- 1: Burning ice: Methane, released by heating, Inset: clathrate structure. **Source-** United States Geological Survey].

2.1 Structure and composition

The methane clathrate hydrate composition is $4(CH_4)23(H_2O)$, or 1 mole of methane for every 5.75 moles of water, corresponding to 13.4% methane by mass, although the actual composition is dependent on how many methane molecules fit into the various cage structures of the water lattice. The observed density is around 0.9 g/cm3, which means that methane hydrate will float to the surface of the sea or of a lake unless it is bound in place by being formed in sediment [18]. One litreof fully saturated methane clathrate solid would therefore contain about 120 grams of methane gas at 0 °C and 1 atm. In 2003, a claymethane hydrate intercalate was synthesized in which a methane hydrate complex was introduced at the interlayer of a sodium rich montmorillonite clay [20].

2.2 Natural deposits

Methane clathrates are very much restricted to the shallow lithosphere. Furthermore, necessary conditions are found only in either continental sedimentary rock in Polar Regions where average surface temperatures are less than 0 °C; or in oceanic sediment at water depths greater than 300 m where the bottom water temperature is around 2 °C. In addition, deep fresh water Lake Baikal, Siberia [21]. Continental deposits have been located in Siberia and Alaska in sandstone and siltstone beds at less than 800 m depth. Oceanic deposits can occur within the sediments at depth or close to the sediment water interface. They may cover even larger deposits of gaseous methane [22]. The Methane hydrate phase diagram is shown in **Figure-2**.

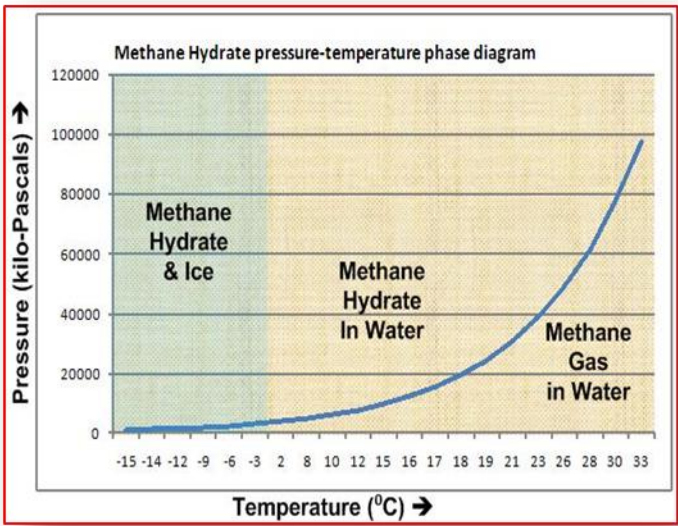

Figure- 2: Methane hydrate phase diagram.

2.3Oceanic deposits

There are two distinct types of oceanic deposit. The most common is dominated which is greater than 99% by methane contained in a structure I clathrate and generally found at depth in the sediment. Here, the methane is isotopically light which indicates that it is derived from the microbial reduction of CO_2. The clathrates in these deep deposits are thought to have formed in situ from the microbially produced methane [23]. Since methane hydrates are more stable in fresh water than in salt water. In the less common second type found near the sediment surface i.e. longerchain hydrocarbons which is less than 99% methane) contained in a structure II clathrate. Carbon from this type of clathrate is isotopically heavier and is thought to have shifted upwards from deep sediments, where methane was formed by thermal decomposition of organic matter [24]. The methane in gas hydrates is dominantly generated by microbial degrading organic matter in low oxygen environments. Organic matter in the uppermost few centimetres of sediments is first attacked by aerobic bacteria, generating CO_2, which escapes from the sediments into the water column. Below this region of aerobic activity, anaerobic processes take over, including, successively with depth, the microbial reduction of nitrite/nitrate, metal oxides, and then sulfates are reduced to sulfides. Finally, once sulfate is used up, methanogenesis becomes a dominant pathway for organic carbon re-mineralization. Gas hydrate bearing sediment and specific structure of a gas hydrate piece are shown in **Figure-3** and **4** respectively.

Figure-3: Gas hydrate bearing sediment

Figure 4: Specific structure of a gas hydrate piece

In some regions (e.g., Gulf of Mexico) methane in clathrates may be derived from Thermal degradation of organic matter, dominantly in petroleum [24].

2.4 Methane Hydrate Formation

The methane which eventually ends up trapped as hydrate compounds comes from micro-organisms that produce methane as a byproduct of consuming buried organic materials. The amount and rate of hydrate accumulation is determined by the methane supply. There are two sources of methane that contribute to hydrate formation in a defined zone of clathrate stability know as the **Hydrate Stability Zone (HSZ)**. The two methane sources include in situ methane generation within the HSZ and deep methane influx. For deep methane influx, natural gases like methane are produced by bacteria that decompose carbon-rich organic sediments that are buried deep within marine sediment layers, and this process provides a relatively constant influx of deep methane gas that is 99.99% pure CH_4. Trace impurities present in the clathrates include the gases Ethane, Propane, Carbon Dioxide, Nitrogen, and Hydrogen Sulfate. These trace gases including larger amounts of CH_4 are also produced by in situ conversion of biomass to methane within the HSZ. Clathrate formation is favoured in coarse sediments as opposed to fine grained sediments. When methane gas enters the HSZ, it dissolves into the pore spaces between and within sediment grains where it exists in three phases [24]. Methane within the HSZ can exist as a free gas, dissolved in solution, or as a solid hydrate. This is because the triple point for these three phases exists at the HSZ by definition. Within the HSZ, methane clathrates are most stable on the ocean floor; however, clathrate crystals are very seldom found here due to the consumption of methane by oxidation reactions with sulfate ions present in seawater. Sulphates react with methane by the reaction:

$$\mathbf{CH_4 + SO_4^{-2} \longrightarrow HS^- + HCO^{3-} + H_2O}$$

whereby any methane present within reach of flowing seawater will be oxidized to the hydrosulphide anion and be removed from the system [25]. **Figure-5** represents the Hydrate stability zone (HSZ) in subsea sediments. The gas trapped within the clathrate has little effect on the clathrate's properties [25].

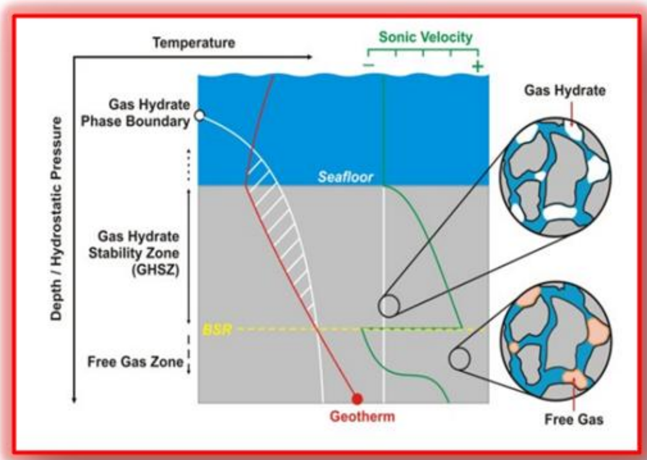

Figure-5: Hydrate stability zone (HSZ) in subsea sediments.

2.5 Clathrate Hydrate Detection

There are many characteristics of hydrate beds that aid in their 3
detection. Cores of marine sediment are taken and the pore water is analyzed for salinity, composition, electrical 4
resistivity, and radioisotope abundances. One of the main 5
isotopes used in methane hydrate detection is ^{129}I. The reason why Iodine is because a good tracer of gas hydrates is because there is a strong correlation with Iodine that is released by the degradation of organic matter and hydrocarbons that are produced by the same process. The evolution of methane and Iodine in deep anoxic sediments will enrich sediment pore water in I relative to seawater, and this makes I a good tracer of organic material flux [26]. Darcy's Law

$$q = -K\,(dh/dl)$$

Where q = discharge

K= hydraulic conductivity constant

is also used to detect methane hydrate formation because the formation rate is determined by the pore fluid migration rate within marine sediments [27]. The coarse sediments that favour methane hydrate formation because the coarse sediments have higher porosity values. This affects the value of K which is the hydraulic conductivity constant. The flow paths that the methane and iodine take from their sources to a depositional hydrate bed can then be determined by extensive core studies and carefully application of Darcy's Law. Moreover, methane hydrate beds may be located by the anomalous heat signature they produce. The formation is an exothermic process and the heat that is evolved is mainly transported by convection and advection. The heat evolved by hydrate formation is given by the equation:

$$\Delta H = T_k.\ \Delta V.\ (dP/dt)$$

Where ΔH = change in enthalpy

T_k= temperature in Kelvin

(dP/dt)= Slope of phase line

One implication of the equation is that as T_k increases from 273K to 313K [24], we see the value for for H increase three to four times. Therefore, gas hydrate beds are often detected thermally by the latent heat of crystallization

. HYRATE AS ENERGY POTENTIAL

Before the gas hydrate discoveries in the last decade, gas hydrates were studied primarily for safety reasons in the oil industry. Methane hydrate beds often occur in the same regions as oil and natural gas reservoirs and it was common for gas hydrates to clog wells and pipelines creating an explosion hazard to the people and property involved in oil extraction. One cubic metre of the compound releases about 160 cubic metre of gas making it a highly energy intensive fuel. Marine gas hydrates have the potential to damage equipment by clogging [25]. Gas hydrates can also occur in tanks and pipes containing refined natural gas if there is any water present therefore, it is very essential to dry any quantity of natural gas prior to the storage or transportation. Methane hydrate fields are almost always more accessible than oil and natural gas reservoirs located deep underground. In addition to marine settings, they have even been found in lakes and inland seas such as Lake Baikal and The Black Sea [25]. A major advantage of these locations is that the infrastructure for natural gas processing is in place from the oil industries already working up there extracting oil and natural gas. This definitely decreases the initial investment that would be required to start harvesting clathrate gas reserves. Another significant fact that makes methane a good fuel source is that it has about 80% the heat content of crude oil which is much better than most other alternative energy sources. Moreover, the combustion reaction for methane is much cleaner than most other hydrocarbon fuel sources. Methane hydrate could be the next energy, "**Game**

Changer", as it is believed that these hydrates as a whole constitute the resources equal the coal and natural gas resources existing in the whole world. From all these above, it is clear that methane hydrates are becoming a more and more attractive alternative to oil and make the hydrate serves as energy potential. Methane hydrate will certainly plays a significant role in our future energy demands.

4. HYDRATES IN NATURAL GAS PROCESSING

Methane clathrates are also usually formed during natural gas production operations when liquid water is condensed in the presence of methane at high pressure. It is known that larger hydrocarbon molecules like ethane and propane can also form hydrates but longer molecules like butane and pentane etc. can't fit into the water cage structure and tend to destabilize the formation of hydrates. Once formed, hydrates can block pipeline and even processing equipment. They are usually removed by reducing the pressure, heating them or dissolving them by chemical means e.g. Methanol is usually used as chemical. Preventive cautions must be taken to ensure that the removal of the hydrates is carefully controlled because of the potential for the hydrate to undergo a phase transition from the solid hydrate to release water and gaseous methane at a high rate when the pressure is reduced. The rapid release of methane gas in a closed system can result in a rapid increase in pressure [18].

4.1 Effect of Hydrate Phase Transition during Drilling

When drilling in oil-gas bearing formations submerged in deep water, the reservoir gas may flow into the well bore and form gas hydrates owing to the low temperatures and high pressures found during deep water drilling. The gas hydrates may then flow upward with drilling fluid (mud) or other discharged fluids. When the hydrates rise, the pressure in the annulus decreases and the hydrates dissociate into gas and water. The rapid gas expansion ejects fluid from the well, reducing the pressure further which leads to more hydrate dissociation and further fluid ejection [28]. The following includes the some measures which reduces the risk of the hydrate formation:

- High flow rates which limit the time for hydrate formation [30].
- Appropriate measures to be taken regarding the line flow when hydrate plugging occurs inside the pipeline [30].
- Monitoring of well casing after it is shut in. The pressure rises while gas diffuses through the reservoir to the bore hole; The pressure rate rise exhibit a reduced rate of increase while hydrates are forming [30].
- Additions of energy i.e. the energy liberated by setting cement used in well completion can raise the temperature and convert hydrates to gas [30].
- dditional care in measuring when gas production rates are low and the possibility of hydrate formation is higher than at relatively high gas flow rates [30].

4.2 Clathrate Recovery

At sufficient depths, methane complexes directly with water to form methane hydrates from a deepwater oil well 1,500 m below sea level to capture escaping oil [29] dome over the largest of the well leaks and piping it to a storage vessel on the surface. **Figure-6** describes the oil containment domes, forming upsidedown funnels in order to pipe oil to surface ship.

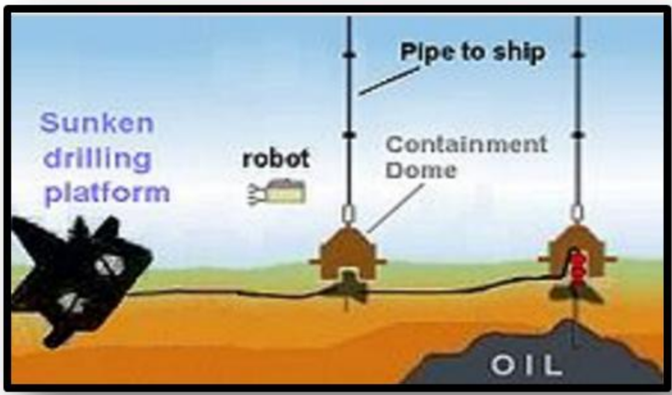

Figure-6: represents the diagram of oil containment domes, forming upside-down funnels in order to pipe oil to surface ship.

5. EXTARCTION TECHNOLOGY

The methane in gas hydrates is commonly generated by bacterial degradation of organic matter in low aerobic environments. Organic matter in the uppermost few cm of sediments is first attacked by aerobic bacteria, generating CO_2 which escapes from the sediments into the water column. Clathrates occur wherever it is cold enough or the pressure is high enough, to make solid ice with methane inside.Because of the requirements of pressure and temperature and because of requirement of relatively large amounts of organic matter for bacterial methanogenesis, clathrates are mainly restricted to two regions:

- High latitudes (permafrost) and
- Along the continental margins in the oceans.

These hydrate beds are very extensive and although there may be large volumes of proven trapped gas reserves. A major problem is that the hydrate density of any particular location is usually not high. While the direct collection of solid methane hydrates would be impractical due to low unit per volume concentration. Several ideas have been postulated for the extraction of methane from hydrate beds [25]. All methods rely on creating a slow controlled dissociation process that will lead freed gas to a drilled bore hole. First of all, any possible extraction site will have to be extensively well studied and extraction techniques would have to be proven safe, efficient, cost effective, and environmentally friendly. There are basically three methods already existing in the literature till date for collecting the gas hydrate. These are:

1. Gases may be collected by thermal stimulation. An influx of hot water or steam would partially melt the hydrate beds in ocean sediments or in permafrost regions. The hot fluids would be pumped down into the hydrate layers and the liberated gases would flow to the bore hole where they ascend through the pipe up to the surface. An advantage of this method is that it is quite simple and would be conceivably easy to do. However, the major disadvantage even is that heating the fluids to pump underground would be cost prohibitive and might not reach deeper hydrate sediments [25].
2. Another method is depressurization of hydrates in sediment beds. This would be done by drilling deep into hydrate beds where methane can exist in the free gas stage before being converted to hydrates. The concept behind this is that a change in the local pressure gradient within the sediment beds will cause the gases to flow freely to a well head. This strategy could be the easiest way to collect hydrate gases [25].
3. An alternative method purposes to collect hydrate gas by the injection of an inhibiting fluid into sediment beds via a well head. The inhibiting fluid may consist of solutions of methanol, ethanol, glycol, or brines and these fluids work to dissociate gas hydrates by altering the chemical composition of the local pore water to no longer favour hydrate stability. These chemicals would lower the freezing point of water in the vicinity, free trapped gases, and the gases would again be collected by the same well head. The most interesting application of the inhibitor injection process is that carbon dioxide could possibly be used as a dissociant [25].

6. DRAWBACKS OF CLATTHARATES HYDRATES

There are so many positive applications of gas hydrate but there are certain negative exists as well. The major drawbacks of gas hydrate are as follow:

6.1 The drawbacks of clathrate hydrates: pipeline plugging

The formation of gas hydrates was responsible for blocking pipelines and machinery processing as well [7]. Considering the significant economic risks in the gas and oil industry, a great deal of research has been conducted by the petroleum industries in order to inhibit this phenomenon. In fact, hydrate propagation tends to gradually form a plug that separates the pipe into two pressure sections: a high pressure section between the well and the plug and a second section at low pressure between the plug and the recovery division. In the upstream section, a pipe blast can occur due to the pressure rise. The plug can also behave as a projectile that destroys the pipe when the pressure difference between the upstream and downstream sections increases. Both events can put personnel safety and damage production equipment [10].

6.2 Clathrate Hydrates as a Possible Energy Game Changer: An Environmental Dilemma

The important amounts of gas hydrates in the Earth's crust might be considered as a new source of sustainable energy [31]. Gas hydrate deposits principally considered as the result of a permanent migration of natural gases throughout Earth fractures and are mainly distributed offshore due to the high pressure and low temperature conditions at the seabed permafrost [32, 33]. Nevertheless, fossil fuel resources are currently sufficient to face worldwide energy needs and thus, gas-hydrate exploitation is dedicated to being a distant prospect especially for offshore hydrates [34]. Even though they are considered as the main hydrocarbon source for the future. Gas hydrate deposits might represent a real threat to the environment. Indeed, when considering offshore hydrates as a global methane reservoir, exploitation of these sediments in unfavourable circumstances could drastically modify the marine ecosystem and even generate underwater gas blowouts [35].

7. THE BENEFITS OF CLATHRATE HYDRATES

7.1 Natural gas storage and transportation

Gas capture by means of methane hydrates has been implemented for storage and transportation of natural gases [36]. This new process involves hydrate production, transportation to the place of use and gas recovery by dissociation of the hydrate structure [37]. The first step is generally achieved by mixing gas and water under hydrate formation temperature and pressure conditions (275–283 K, 8–10 MPa) [37]. This storage and transportation process is possible only due to the met stability characteristics of methane hydrates [38]. In order to increase the hydrate formation rate, surfactants can be added to the solution [39-41].

7.2 Cool Storage Application

Research going on refrigerating systems with a reduced impact on the environment has become urgent. Secondary refrigeration can be a promising alternative to face this problem by the containment of a reduced load of primary refrigerant i.e. hyroflurocarbons (HFCs) in an engine room. The refrigerating capacity delivered to the secondary refrigerant is then transported towards the places of use [42-45]. Clathrate hydrates were favourably reconsidered at a later date specifically for cold storage. Since their large heat of melting was confirmed by various authors [46-48]. Moreover, since their phase change temperature is above the freezing point of water [49-53], the use of hydrate energy is very much relevant for the field of air conditioning.

7.3 Carbon Dioxide Sequestration and Separation Processes

About more than 50% of the enhanced greenhouse gas effect is due to carbon dioxide emissions [54]. Such process can be performed by releasing the CO_2 in water using a process adapted to the injection depth [55, 56]. Down to sea approximately 400 meters gaseous CO_2 is injected and then trapped by dissolution in the water [57]. Between 1000 and 2000 m in deep sea water, CO_2 in the liquid state diffuses and also dissolves in the ocean [58]. CO_2 hydrates can appear from 500 to 900 m in CO_2-rich seawater and then sink, owing to their density [59].

Desalination or gas–liquid fractionation also use hydrates in a very particular beneficial manner. Desalination or gas–liquid fractionation also use hydrates in a beneficial manner. The feasibility of seawater desalination by means of hydrates was demonstrated but the process was not developed industrially since it was not economically viable [60]. This process is based on gas hydrate formation by refrigerant injection in seawater. After separating the hydrate, pure water is recovered by heating the hydrates.

8. CLATHRATES AS A CAUSE OF CLIMATE CHANGE-POTENTIAL ENVIROMEMTAL IMPACTS

While methane hydrate resources may appear to be an enormous boon to energy hungry nations like Japan, it is widely considered that developing methane hydrates could have a significant detrimental effect on the climate change. During the formation of gas hydrates, methane and water become immobilized within the sediment pore spaces. Because of the presence of these solids, the sediment cannot become consolidated because the water cannot be expulsed. Sedimentation occurs. Cementation of the sediments does not occur when pore spaces are filled with hydrates. Gas hydrate rich sediments are thus cemented by the hydrate ice which may occupy much of the sedimentary section. But which are not stable when the temperature rises or the pressure. In general, rising temperatures have more effect than falling pressure. If temperatures of ocean waters rise, hydrates will no longer be stable and will disintegrate into a liquid water and gas. This could lead to the development massive undersea landslides. With the landslides, more gas could escape. Methane is a powerful greenhouse gas. Despite its short atmospheric half life of 7 years, methane has a global warming potential of 86 over 20 years and 34 over 100 years [61-63]. The sudden release of large amounts of natural gas from methane clathrate deposits has been hypothesized as a cause of past and possibly future climate changes. Ongoing global warming already caused slight warming of ocean water at the depths that gas hydrates occur. Thus it could trigger release of methane and thus cause more global warming. Methane released within sea water could also become oxidized within the oceans and use up oxygen in the process. This would cause a deficiency of oxygen within the deeper waters layers of oceans, which cannot pick up oxygen from the atmosphere easily and definitely be disastrous for aquatic life.

9. TECHNICAL CHALLENGES

Methane hydrates had never been tapped as a source of energy to meet increasing global demands. It has generally been considered that other sources of fossil fuels and conventional oil and gas have been easier and cheaper to access. Now we are in a position to make out the success to complete the global energy demand by clatharates but there are certain technical challenges in accessing the gas hydrates. Quite apart from reaching them at the bottom of deep ocean, there are the potentially serious issues of destabilizing the seabed which can lead to submarine landslides.

- A greater potential threat is methane escape. Extracting the gas from a localized area of hydrates does not present too many difficulties, but preventing the breakdown of hydrates and subsequent release of methane in surrounding structures is more difficult. And escaping methane has serious consequences for global warming. Recent studies suggest the gas is 30 times more damaging than CO_2. These technical challenges are the reason why as yet, there is no commercial scale production of methane hydrate anywhere in the world till now.
- Also there are some others challenges associated with producing natural gas. The biggest issue is transportation. Natural gas is usually transported by pipeline or tanker truck as a liquid. Liquefied Natural Gas (LNG) has the danger of exploding due to an ignition source or simply a pressure rupture. LNG has the added disadvantage that it has to be liquefied in order to economically transport quantities of it and that process is time-consuming and costly.
- Large methane releases from marine sediments do occur on smaller scales and that these small methane bubble releases can pose a threat to ships and airplanes in areas of high methane concentration. Correspondingly, aircraft engines have been shown to suddenly stall and fail in atmospheric concentrations of methane as low as 1%.

Therefore, these facts have led some people to suspect that the cause of the infamous Bermuda Triangle ship and airplane disappearances was at least partially due to methane eruptions from the seabed [64].

10. CURRENT RESEARCH STATUS

The production methods have so far been explored for the recovery of natural gas aim at thermodynamically destabilizing the reservoir environment to provoke the release of the entrapped gas hydrate. They have been investigated experimentally as well as numerically. However, they have not yet been used for commercial production of natural gas hydrates due to existing above said technical and economic issues. Also research studies is going on the current topic and additional experimental data which will help in methane-carbon dioxide molecular gas exchange in hydrate-bearing sediments. Moreover, researchers are also emphasizing on the importance of fully knowing the thermodynamics and kinetics of the formation and dissociation of this mixed hydrate and of the conversion process in porous media.

11. CONCLUSIONS

This paper represents a brief review of the studies that have been performed within the methane hydrate to till date. As this paper highlights, such studies are even more essential in these days and age, as we need to quickly discover and exploit new sources of energy in a sustainable and energy-efficient manner because world is addicted to hydrocarbons as they represent the abundant source to fuel industrial development. An emphasis should be put on these hydrates which will surely lead to an improved understanding of our plant geology and potentially unlock new solutions in the production, transportation and storage of this new form of solid ice. Also it would help in finding or open up the untapped reserves of natural gas. More recently, they were encountered in refrigeration where their crystallization occurred in expansion valves. However, by overcoming these drawbacks it makes us possible to acquire substantial knowledge of hydrates including their existing conditions, their crystalline structure and their ability to store gas. Cold storage using hydrates as phase change materials is a promising application in secondary refrigeration. In a nutshell, even if many studies will focus on the disturbing aspect of hydrates, the positive prospects would be numerous and encouraging. More work has to be done the production technology that achieves controlled release of the methane from the ice into the production well, hence minimizing the risk of gas escaping into the atmosphere. In order to scientifically conclude which production method is the best and effective, we have to put more emphasis on the study of physical properties of the methane hydrate itself and state and physical properties of methane hydrate- bearing layers and also on the establishment of the analytical methods because there is no methods available for measuring these properties till date which is accepted on a global scale. All of the production has either been small scale or experimental. Therefore, for extracting the gas some specialized equipment has to be used which will drill into the well and depressurize the hydrate deposits causing the methane to separate from the ice. Hence further research on the topic is encouraged to make out the solution to these challenges and to make it more commercially viable. Overall, this review article may therefore serve as a challenge to researchers to continue developing more techniques for the easy access of clathrate hydrates.

12. FUTURE PROSPECTS RECOMMENDED

The world's demand for energy continues to increase rapidly and global energy consumption is expected to rise nearly 40% between 2014 and 2035. Among all the fossil fuels, gas demand is growing fastest and is increasingly being used as a cleaner alternative to coal for power generation as well as in other sectors. Any potential new source of gas production is therefore likely to be given considerable attention by both industry and government as well. Therefore, Methane hydrates may represent the world's largest source of untapped fossil energy. They are believed to be a larger hydrocarbon resource than all of the world's oil, natural gas and coal resources combined. Yielding commercial quantities of natural gas at an affordable price presents numerous challenges till now. This clatharate hydrate field is a vast and emerging field and it requires research at every stage of technology development. If the technology to commercially extract gas from hydrates is developed, the implications for global energy markets are staggering.

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CONFLICT OF INTEREST

Author declares no conflict of interest.

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